

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets

W1037-02 (8) 7410



(11)

EP 0 930 338 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:

12.12.2001 Bulletin 2001/50

(51) Int Cl.7: C08L 27/12, C08L 33/16,
C08L 101/00

(21) Application number: 97940357.3

(86) International application number:
PCT/JP97/03218

(22) Date of filing: 12.09.1997

(87) International publication number:
WO 98/13421 (02.04.1998 Gazette 1998/13)

(54) RESIN COMPOSITION

HARZZUSAMMENSETZUNG

COMPOSITION DE RESINE

(84) Designated Contracting States:
DE FR GB IT

(30) Priority: 25.09.1996 JP 25279196
11.12.1996 JP 33089196

(43) Date of publication of application:
21.07.1999 Bulletin 1999/29

(73) Proprietor: DAIKIN INDUSTRIES, LIMITED
Osaka-shi Osaka 530 (JP)

(72) Inventors:

- KITAHARA, Takahiro,
Yodogawa Works of Daikin Ind.
Osaka 566, Osaka 566 (JP)
- YAMAGUCHI, Fumihiko, Yodogawa Works of
Daikin Ind.
Osaka 56 (JP)

- HONDA, Yoshitaka Yodogawa Works of Daikin
Ind. Ltd
Osaka 566 a 566 (JP)

(74) Representative: HOFFMANN - EITLE
Patent- und Rechtsanwälte
Arabellastrasse 4
81925 München (DE)

(56) References cited:
EP-A- 0 460 689 JP-A- 1 123 849
JP-A- 4 020 217 JP-A- 4 076 030
JP-A- 4 085 349 US-A- 4 220 583

- PATENT ABSTRACTS OF JAPAN vol. 012, no.
297 (C-519), 12 August 1988 & JP 63 066256 A
(YOBEO RULON KOGYO KK), 24 March 1988
- PATENT ABSTRACTS OF JAPAN vol. 016, no.
289 (C-0956), 26 June 1992 & JP 04 076057 A
(NTN ENG PLAST CORP), 10 March 1992

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 930 338 B1

Description

FIELD OF THE INVENTION

5 [0001] The present invention relates to a resin composition and a resin molded article produced from said resin composition.

RELATED ARTS

10 [0002] Hitherto, in making a thermoplastic resin resistant to flame, it is known that for the purpose of preventing the dropping at the time of combustion and of reducing, the amount of flame-retardant, fibrillated polytetrafluoroethylene (PTFE) together with a flame-retardant is added to the thermoplastic resin to compound a flame-retardant resin.

[0003] The amount of PTFE added to such flame-retardant thermoplastic resin is an amount which is as low as about 0.1 to 1.0 % by weight, but is sufficient to exhibit the prevention of dropping at the time of combustion.

15 [0004] However, because PTFE does not have affinity for other materials, there is the disadvantage that its addition even in such a small amount significantly lowers the impact strength of thermoplastic resin.

[0005] Further, PTFE is added for the purpose of conferring sliding properties on the thermoplastic resin. The addition amount in this case is varied depending on sliding use and the type of thermoplastic resin. As to low-sliding use, for e.g. CD-ROM tray materials such as in personal computers, PTFE is added in an amount of 2 to 5 % by weight to an acrylonitrile/butadiene/styrene (ABS) resin, and even for gears used in OA (office automation) instruments, PTFE is added in an amount of about 5 % by weight to a polycarbonate resin.

[0006] As to high-sliding use, e.g. in bearing materials, there are also cases where PTFE is added in an amount of 20 to 50 % by weight to polyphenylene sulfide.

20 [0007] Even in cases where PTFE is added in a relatively large amount, there is the disadvantage of reduction in impact strength.

[0008] Further, hitherto, when connectors and sockets used in electrical and electronic parts are produced, a terminal is attached by soldering to a connector resin by passing the terminal through a through-hole. Due to capillarity, the flux used is passed through the through-hole and raised to the terminal. Because acidic components are contained in the flux, they can be the cause of terminal corrosion to cause a contact failure and the like.

30 EP-A-0 460 689 discloses a sliding material composition comprising

(a) 100 parts by weight of a polyphenylene sulfide, and

(b) 5 to 100 parts by weight of a resin mixture of

35 10 % to 90 % by weight of a melt processable fluorine-containing resin and
90 % to 10 % by weight of a polytetrafluoroethylene.

Specific examples of the melt processable fluorine-containing resin are tetrafluoroethylene/perfluoroalkyl vinyl ether copolymers, tetrafluoroethylene/hexafluoropropylene copolymers, tetrafluoroethylene/hexafluoropropylene/perfluoroalkyl vinyl ether copolymers, and ethylene/tetrafluoroethylene copolymers, polyvinylidene fluoride, polychlorotrifluoroethylene. PFA and ETFE are preferred.

40 [0009] JP-A- 63-66256 discloses an aromatic polyether-ketone resin composition comprising five components, i.e. (1) an aromatic polyether ketone resin, (2) a tetrafluoroethylene resin, (3) an injection-moldable fluororesin, (4) an aromatic polyester resin and (5) a calcium compound. It is taught to use tetrafluoroethylene resin and the injection-moldable fluororesin as the fluorine-containing polymer. The injection-moldable fluororesin is a tetrafluoroethylene/perfluoroalkyl vinyl ether copolymer (PFA), a tetrafluoroethylene/hexafluoropropylene copolymer (FEP), an ethylene/tetrafluoroethylene or polyvinylidene fluoride. This document is concerned with good sliding properties of the resin composition.

50 [0010] JP-A-485349 relates to a lubricating rubber composition comprising a synthetic rubber, a thermoplastic fluororesin and a low molecular weight fluorine-containing copolymer. It is taught to use the thermoplastic fluororesin and the low molecular weight fluorine-containing copolymer as the fluorine-containing polymer. The low molecular weight fluorine-containing polymer used is a fluoroolefin polymer such as tetrafluoroethylene (TFE) and a tetrafluoroethylene/hexafluoropropylene copolymer (FEP), a fluoropolyether having a main chain structure: $-C_nF_{2n}-O-$ (n is an integer of 1 to 4), a polyfluoroalkyl group-containing compound (C_2 to C_{20}) having a main chain structure: $CF_3-(CF_2)_n$, or $H(CF_2)_n$.

SUMMARY OF THE INVENTION

55 [0011] An object of the present invention is to provide a resin composition which has excellent impact strength and

repels a flux well.

[0012] The present invention provides a resin composition comprising:

- (a) a fluorine-free thermoplastic resin,
- (b) a fluorine-containing resin which is a homopolymer, modified polymer or core/shell polymer of tetrafluoroethylene, and
- (c) a polyfluoroalkyl group-containing polymer which is (i) a homopolymer or copolymer of polyfluoroalkyl group-containing (meth)acrylate or (ii) a polyfluoroester.

[0013] The resin composition of the present invention may further comprise (d) a flame-retardant.

[0014] The present invention further provides a resin molded article produced from said resin composition.

DETAILED DESCRIPTION OF THE INVENTION

[0015] The fluorine-free resin (a) is a thermoplastic resin having no fluorine atom.

[0016] The thermoplastic resin includes a styrene-type resin (e.g. polystyrene, acrylonitrile/styrene resin (AS), acrylonitrile/butadiene/styrene resin (ABS)); an olefin-type resin (e.g. polyethylene, polypropylene, polymethylpentene); polyvinyl chloride; a carbonate-type resin (e.g. polycarbonate (PC), a PC-type alloy resin such as a polycarbonate-acrylonitrile/butadiene/styrene alloy resin (PC/ABS)); a polyamide-type resin (e.g. nylon, wholly aromatic polyamide); a polyester-type resin (e.g. polybutylene terephthalate, polyethylene terephthalate, wholly aromatic polyester); a polyamide-type alloy resin; a polyester-type alloy resin; an acrylic resin (e.g. polymethyl methacrylate, polyacrylonitrile); polyacetal; polyether ether ketone; and polyphenylene sulfide; modified polyphenylene ether.

[0017] The weight average molecular weight of the fluorine-free resin (a) may be from 1000 to 1,000,000.

[0018] The fluorine-containing resin (b) is a homopolymer, modified polymer or core/shell polymer of tetrafluoroethylene (TFE). The fluorine-containing resin (b) may be fine powder obtained by emulsion polymerization or molding powder obtained by suspension polymerization.

[0019] The modified polymer of tetrafluoroethylene is a copolymer prepared by copolymerizing the following modifying monomers in an amount of 0.001 to 1.0 % by weight (based on the copolymer). The modifying monomers used in the modified polymer include e.g. hexafluoropropylene, trifluoromonochloroethylene, perfluorovinyl ether, and fluoroalkyl ethylene. The core/shell polymer is described in e.g. Japanese Patent Kokai Publication Nos. 154,842/1992, 158,651/1990, 274,711/1990, 247,408/1989, and 312,836/1988.

[0020] The core/shell polymer includes e.g. (i) polytetrafluoroethylene fine particles having an average particle size of 0.05 to 1.0 μm comprising a core made of high-molecular-weight polytetrafluoroethylene that can be fibrillated and a shell made of low-molecular-weight polytetrafluoroethylene that can not be fibrillated and (ii) fine particles having an average particle size of 0.05 to 1.0 μm comprising a core, that is, a polymer made of 99 to 100 % by weight of tetrafluoroethylene and 0 to 1 % by weight of a fluorine-containing olefin copolymerizable with tetrafluoroethylene, and a shell, that is, at least one copolymer selected from the group consisting of ethylene/tetrafluoroethylene copolymers, ethylene/chlorotrifluoroethylene copolymers, tetrafluoroethylene/ethylene/hexafluoropropylene copolymers, tetrafluoroethylene/hexafluoropropylene copolymers, tetrafluoroethylene/perfluorovinyl ether copolymers, tetrafluoroethylene/hexafluoropropylene/perfluorovinyl ether copolymers and vinylidene fluoride/tetrafluoroethylene copolymers.

[0021] The fluorine-containing resin (b) may be low-molecular-weight (e.g. a weight average molecular weight of 1×10^4 to 8×10^5) tetrafluoroethylene homopolymers and modified polymers. *10000 ~ 500000*

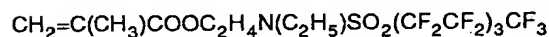
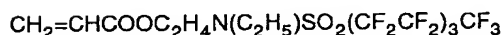
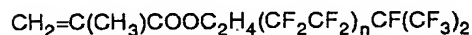
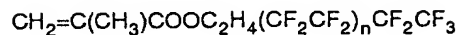
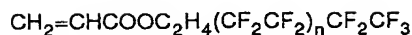
[0022] The fluorine-containing resin (b) may be tetrafluoroethylene/hexafluoropropylene copolymers (FEP), tetrafluoroethylene/perfluorovinyl ether copolymers (PFA), ethylene/tetrafluoroethylene copolymers (ETFE), polyvinylidene fluoride (PVdF), tetrafluoroethylene/ethylene/hexafluoropropylene copolymers, tetrafluoroethylene/hexafluoropropylene/perfluorovinyl ether copolymers, and vinylidene fluoride copolymers. A comonomer copolymerized with vinylidene fluoride in vinylidene fluoride copolymers includes tetrafluoroethylene (TFE), hexafluoropropylene (HFP), chlorotrifluoroethylene (CTFE), trifluoromonochloroethylene (TrFE), and a combination thereof. *1000 ~ 1000000*

[0023] The weight average molecular weight of the fluorine-containing resin (b) may be from 1×10^3 to 1×10^7 .

[0024] The amount of the fluorine-containing resin (b) may be from 0.01 to 100 parts by weight, based on 100 parts by weight of the fluorine-free resin (a). The amount is preferably varied depending on the desired use. For example, in order to confer the dripping prevention properties on the thermoplastic resin, the amount is preferably from 0.1 to 5.0 parts by weight. To confer the sliding properties, the amount is preferably from 2 to 60 parts by weight.

[0025] The polyfluoroalkyl group-containing polymer (c) is (i) a homopolymer of a polyfluoroalkyl group-containing monomer or a copolymer of said monomer and a comonomer copolymerizable therewith or (ii) a polyfluoroester.

[0026] Examples of polyfluoroalkyl group-containing (meth)acrylate are as follows:



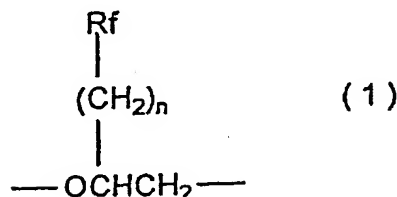
(n = an integer of 1 to 10)

[0027] The number of carbon atoms in the polyfluoroalkyl group may be from 5 to 18. The polyfluoroalkyl group may be a perfluoroalkyl group. In particular, (meth)acrylic ester where the number of carbon atoms in the polyfluoroalkyl group ranges from 8 to 12 is preferable. These are used alone or in combination thereof.

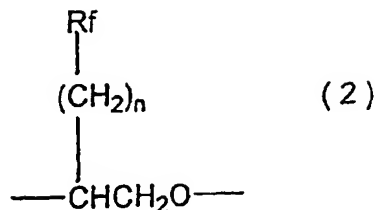
[0028] The comonomer copolymerizable with a polyfluoroalkyl group-containing monomer includes (meth)acrylate alkyl ester, (meth)acrylic acid amide, vinyl acetate, vinyl chloride, styrene, α -methylstyrene, polyoxyethylene (meth)acrylate, and polyoxypropylene (meth)acrylate.

[0029] The polyfluoroalkyl group-containing polymer (c) may also be a polyfluoroester. The polyfluoroesters are polyfluoroalkyl group- and ester group-containing compounds and may be compounds described in Japanese Patent Kokai Publication Nos. 139,696/1978 and 139,697/1978.

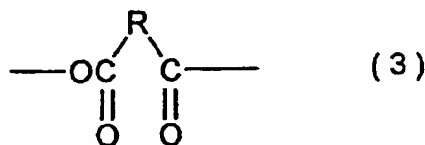
[0030] The polyfluoroesters possess the repeating units represented by formula (1) or (2):



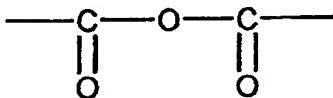
or



wherein Rf is a polyfluoroalkyl group containing 3 to 21 carbon atoms, and n is an integer of 0 or 1, and repeating units represented by formula (3):



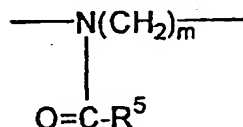
wherein R is a residue remaining after removing the group:



from cyclic anhydride.

[0031] In addition to the repeating units represented by formula (1) or (2) and (3), the polyfluoroesters may, if necessary, have repeating units represented by the formula:

-(OCR¹R²CR³R⁴)- and/or the formula:



wherein R¹, R², R³ and R⁴ each represents a hydrogen atom, an alkyl or aryl group optionally having a substituent group, R⁵ represents a hydrogen atom, an alkyl or aryl group optionally having a substituent group, and m is an integer of 2 or 3.

[0032] The weight average molecular weight of the polyfluoroalkyl group-containing polymer (c) may be from 1,000 to 1,000,000.

[0033] The amount of the polyfluoroalkyl group-containing polymer (c) may be from 0.001 to 50 parts by weight, preferably 0.01 to 10 parts by weight, e.g. 0.1 to 5 parts by weight, based on 100 parts by weight of the fluorine-free resin.

[0034] Typical examples of the flame-retardant (d) are compounds containing Group 5B elements in the periodic table, such as nitrogen, phosphorus, antimony and bismuth, and compounds containing Group 7B halogen elements. The halogen-containing compounds include aliphatic halogen-containing compounds, alicyclic halogen-containing compounds, aromatic organic halogen-containing compounds such as bromine-type compounds, for example, tetrabromobisphenol A (TBA), decabromodiphenyl ether (DBDPE), octabromodiphenyl ether (OBDPE), TBA epoxy/phenoxy oligomers and brominated crosslinked polystyrene, and chlorine-type compounds, for example, chlorinated paraffin and perchlorocyclopentadecane. The phosphorus-containing compounds include e.g. phosphate esters and polyphosphate salts. The antimony-containing compounds are used preferably in combination with halogen compounds

and include e.g. antimony trioxide and antimony pentaoxide. Besides, aluminum hydroxide, magnesium hydroxide, and molybdenum trioxide can also be used. The type and the addition amount of the flame-retardant (d) can be arbitrarily selected and are not limited to those exemplified.

[0035] The amount of the flame-retardant (d) may be from 0 to 40 parts by weight, e.g. 0.01 to 30 parts by weight, based on 100 parts by weight of the fluorine-free resin (a).

[0036] Further, additives known in the art, such as UV absorbers, antioxidants, pigments, molding auxiliary agents, calcium carbonate and glass fibers, may be added, if necessary, to the resin composition of the present invention.

[0037] The means of blending the resin composition of the present invention includes, but is not limited to, single-screw extruders, twin-screw extruders, open rolls, kneaders and mixers.

[0038] The resin composition of the present invention can be used as flame-retardant resin and sliding members used in OA (office automation) instruments (e.g. housing materials for personal computers, facsimile machines, copying machines and printers, chassis materials, CD-ROM tray materials, bearing sliding members, paper-sending materials and key board materials).

[0039] The resin composition of the present invention can also be used as a resin which has sliding properties, is resistant to abrasion resistance, and dissolves creak sounds in e.g. electric appliances (e.g. air conditioners and videotape recorders), cameras and automobile parts.

[0040] It was further found that a resin molded article excellent in water- and oil-repellency can be obtained by adding the polyfluoroalkyl group-containing polymer having low surface tension to the resin composition of the present invention. It was found that the water- and oil-repellency can be further improved by thermally treating the resin molded article at 70 to 130 °C and that the resulting article can also be used in kitchen utensils, bathroom articles, toilet equipments (e.g. washbasin, bathtub and sanitary container).

[0041] Specific examples of the molded articles include:

bathroom articles (a bathtub, an interior portion of a unit bath, a washbasin, a bucket, a soap stand, a soap dish, a shampoo rack, and a chair);
kitchen utensils (a ceiling door in a system kitchen, a sink, a washbasin, a triangular corner, a draining bucket, and a detergent rack);
toilet equipment (a toilet seat, a paper holder, a toilet corner, a water tank, a towel rack, a toilet brush and its casing);
hygienic nursing articles (a portable toilet, a handy toilet seat and a handrail);
washroom equipment (a washstand, a tube stand, a tooth-brushing cup, a tray, a towel rack, and a miller stand);
cleaning equipment (a bucket, compost, a tub, and a garbage can);
closet equipment (a cloth case, a caster rack, and a hook); and
articles for babies (a bedpan, a toilet seat for children, a baby sink, a stool, and a baby bottle).

[0042] The resin composition of the present invention can be used in portions liable to dirt in home (e.g. a sash, a floor material sheet, a wall paper, a chemical tatami mat, a cabinet for TV and radio, an audio rack, and an inner cover in a refrigerator).

[0043] The time for thermal treatment may be 30 minutes to 20 hours, e.g. 1 to 3 hours.

[0044] Further, the resin composition of the present invention can be used as a resin for preventing flux from raising in materials (particularly polybutylene terephthalate resin) of electrical or electronic connectors. If the resin composition of the present invention is used as a connector member, it is possible to prevent flux from raising to a terminal when the terminal is passed through a through-hole in order to solder the terminal.

[0045] The resin composition of the present invention can be molded to give a molded article. Molding can be conducted by injection molding, compression molding, transfer molding, extrusion molding, blow molding and calendar molding.

EXAMPLES

[0046] Hereinafter, the term "part" refers to part by weight unless otherwise specified.

[0047] The tests in the present invention were conducted in the following manner.

Impact Energy

[0048] As an impact energy value, the average of 10 measurements of an unnotched specimen was determined at a hammer capacity of 588 N/cm (60 kgf·cm) at an impact rate of 3.45 m/sec. in a Charpy Impact testing machine (manufactured by Toyo Seiki Co., Ltd.).

Flame Retardance

[0049] Flame retardance was measured in accordance with United States UL (underwriters' laboratories) 94 combustion test, V class.

Contact Angle

[0050] A contact angle of water and n-hexadecane on the surface of a molded article was determined using a contact angle measuring instrument (manufactured by Kyowa Kaimen Kagaku K. K.).

Friction Coefficient

[0051] An abrasion wear volume of a sample against an ABS resin (Diapet ABS1002, manufactured by Mitsubishi Rayon Co., Ltd.) was determined at a loading of 1000 g/cm², at a rotation rate of 0.3 m/sec. for a measurement time of 24 hours in a thrust abrasion testing machine (manufactured by Orientec K.K.). A specific abrasion wear was calculated from the abrasion wear volume according to the following equation:

$$\text{Specific abrasion wear} = W/P \cdot V \cdot T$$

wherein

W is an abrasion wear volume (cm³),

P is a loading (kg),

V is a rotation rate (m/sec) and

T is a measurement time (hr).

Flux Barrier Properties

[0052] A molded article was provided with a small through-hole for insertion of a lead terminal, and this molded article was immersed in 80 weight-% solution of commercial flux (Solderite CF-220VH) in isopropyl alcohol and then the lead terminal was inserted into the through-hole, and whether the flux was raised to the lead terminal or not was evaluated with eyes.

O: The flux did not raise to the lead terminal.

X: The flux raised to the lead terminal.

Synthesis Example 1

[0053] A 2 L four-necked flask was charged with 300 g of polyfluoroalkyl acrylate [$\text{CH}_2=\text{CHCOOC}_2\text{H}_4(\text{CF}_2\text{CF}_2)_n\text{CF}_2\text{CF}_3$ (average of n: 3.65)], 300 g of stearyl methacrylate [$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_{17}\text{H}_{35}$], 600 g of isopropyl alcohol (solvent), and 30 g of laurylmercaptan (solvent), and the atmosphere in the flask was replaced by nitrogen. After the temperature was raised to 70°C, 4 g of azobisisobutyronitrile was added to it, and the mixture was polymerized for 15 hours with stirring. Thereafter, the reaction mixture was introduced into a large amount of methanol to form precipitates, and the precipitates were separated by filtration and dried at 40°C under reduced pressure whereby 538 g of a polyfluoroalkyl group-containing polymer was obtained. This polymer was comminuted in a mortar to give powder.

Synthesis Example 2

[0054] The same procedure as in Synthesis Example 1 was repeated except that the amount of polyfluoroalkyl acrylate was 210 g, the amount of stearyl methacrylate was 90 g, and 600 g of n-perfluorohexane was used in place of 600 g isopropyl alcohol, whereby 261 g of polyfluoroalkyl group-containing polymer powder was obtained.

Example 1

[0055] 100 parts of an ABS resin (thermoplastic resin) [ABS15, manufactured by Japan Synthetic Rubber Co., Ltd.], 22.5 parts of brominated epoxy resin (flame-retardant) [YDB-408, manufactured by Tohto Kasei K. K.], 7.0 parts by weight of antimony trioxide (flame-retardant) [ATOX-S, manufactured by Nihon Seiko Co., Ltd.], and 0.39 part of powder

in which polytetrafluoroethylene fine powder [Polyflon F-201, manufactured by Daikin Industries Ltd.] and the polyfluoroalkyl group-containing polymer prepared in Synthesis Example 1 had been preliminarily blended at the weight ratio of 2 : 1, were mixed at room temperature for 10 minutes in a tumbler, and compounded and pelletized in a twin-screw kneading extruder to give a flame-retardant ABS resin composition.

[0056] The conditions for the kneading extrusion were an extrusion temperature of 210°C, a screw revolution of 130 rpm and a feeding of 8 kg/hr.

[0057] Then, an UL94 combustion specimen (12,7 cm (5 inches) in length, 1,3 cm (1/2 inch) in width and 0,16 cm (1/16 inch) in thickness) and a Charpy impact specimen (12,7 cm (5 inches) in length, 1,3 cm (1/2 inch) in width and 0,31 cm (1/8 inch) in thickness) were prepared in an injection molding machine [SG50, manufactured by Sumitomo Heavy Industries, Ltd.]. Then, the UL94 combustion test and the Charpy impact test were conducted. The results are shown in Table 1.

Comparative Example 1

[0058] The same procedure as in Example 1 was repeated except that the polyfluoroalkyl group-containing polymer prepared in Synthesis Example 1 was not used. The results are shown in Table 1.

Example 2

[0059] 100 parts of ABS resin (thermoplastic resin) [ABS15, manufactured by Japan Synthetic Rubber Co., Ltd.], 4.0 parts of a polytetrafluoroethylene low-molecular weight polymer [Lubron L-5, manufactured by Daikin Industries Ltd.] (weight average molecular weight of about 300,000), and 2.0 parts of the polyfluoroalkyl group-containing polymer prepared in Synthesis Example 1 were mixed in the same manner as in Example 1 to give an ABS resin composition.

[0060] A Charpy impact test specimen (12.7 cm (5 inches) in length, 1.3 cm (1/2 inch) in width, and 0.31 cm (1/8 inch) in thickness) and an abrasion test specimen (a molded disk having an outer diameter of 4.6 cm, an inner diameter of 1.2 cm, and a thickness of 0.3 cm) were prepared in the injection molding machine in the same manner as in Example 1, and the Charpy impact test and the abrasion test were conducted. The results are shown in Table 1.

[0061] Further, the Charpy impact test specimen was thermally treated at 90°C for 1 hour and then examined for contact angle with water and n-hexane. The results are shown in Table 1:

Comparative Example 2

[0062] The same procedure as in Example 2 was repeated except that the polyfluoroalkyl group-containing polymer prepared in Synthesis Example 1 was not used. The results are shown in Table 1.

Example 3

[0063] The same procedure as in Example 2 was repeated except that a core/shell polymer of polytetrafluoroethylene described in Example 2 in Japanese Patent Kokai Publication No. 154,842/1992 was used in place of the polytetrafluoroethylene low-molecular weight polymer. The results are shown in Table 1.

[0064] The core/shell polymer of polytetrafluoroethylene was produced in the following manner. A 6 L stainless steel autoclave was charged with 2960 mL of de-ionized water and 1.0 g of ammonium perfluorooctanoate, and while the mixture was heated at 55°C, the atmosphere in the system was replaced 3 times by a nitrogen gas and 2 times by a tetrafluoroethylene (TFE) gas to remove oxygen, and the system was kept at an internal pressure of 0,78 MPa (8 kgf/cm²) with TFE with stirring at 250 rpm and at an internal temperature of 55°C. An aqueous solution of 30 mg (10 ppm based on total amount of water) of ammonium persulfate (APS) in 20 mL of water was introduced by compressing it with TFE, and the internal pressure of the autoclave was made 0,88 MPa (9 kgf/cm²). The reaction proceeded acceleratively, during which the system was kept at a reaction temperature of 55°C with stirring at 250 rpm. TFE was continuously fed so that the internal pressure of the autoclave was kept at 0.88 ± 0.05 MPa (9 ± 0.5 kgf/cm²). Once TFE consumed during the reaction reached 390 g after addition of the initiator, the feeding of TFE and stirring were terminated, and the TFE in the autoclave was released.

[0065] Then, while the internal pressure was raised to 0.88 MPa (9 kgf/cm²) by TFE, an aqueous solution of 1800 mg (600 ppm based on total amount of water) of APS in 20 mL of water, and 36 g of 1,2-dichloroethane were compression-introduced. Thereafter, the reaction was initiated again by stirring, and TFE was continuously fed so that the internal pressure of the autoclave was kept at 0.88 ± 0.05 MPa (9 ± 0.5 kgf/cm²). Once 780 g of TFE monomer was consumed in the reaction, the stirring and feeding of the monomer were terminated, and immediately the gas in the autoclave was released to give a normal pressure to terminate the reaction. The weight ratio of the core to the shell in the resulting polymer was 50 : 50. The total reaction time was 20 hours. Ammonium carbonate was added to the

resulting latex, and the mixture was stirred, coagulated, washed, and dried at 140°C for 15 hours to give tetrafluoroethylene core/shell polymer powder.

Example 4

[0066] 100 parts by weight of a polybutylene terephthalate resin (thermoplastic resin) [1401X06, manufactured by Toray], 20 parts by weight of a brominated epoxy resin (flame-retardant) [YDB-408, manufactured by Toto Kasei K. K.], 7 parts by weight of antimony trioxide (flame-retardant) [ATOX-S, manufactured by Nihon Seiko Co., Ltd.], 1.3 parts by weight of polytetrafluoroethylene fine powder [Polyflon MPA FA-500, manufactured by Daikin Industries Ltd.], and 2.0 parts by weight of the polyfluoroalkyl group-containing copolymer prepared in Synthesis Example 2 were preliminarily mixed at room temperature for 10 minutes in a tumbler, and compounded and pelletized in a twin-screw extruder to give a PBT resin composition.

[0067] The conditions for kneading extrusion were an extrusion temperature of 240°C, a screw revolution of 130 rpm and a feeding of 8 kg/hr.

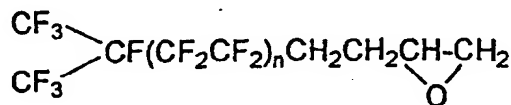
[0068] Then, an UL94 combustion specimen and a Charpy impact specimen were prepared and the tests were performed. Further, a flux barrier test was conducted using the UL94 combustion specimen. The results are shown in Table 1.

Comparative Example 3

[0069] The same procedure as in Example 4 was repeated except that the polyfluoroalkyl group-containing polymer prepared in Synthesis Example 2 was not used. The results are shown in Table 1.

Synthesis Example 3

[0070] 526 g of Rf epoxy shown in the formula:



(n=3.5), 120 g of phenyl glycidyl ether, 238 g of phthalic anhydride and 41 g of acetic anhydride were introduced into a 1.5 L glass reaction vessel and heated to 130°C in an oil bath. After the whole of the mixture was dissolved, 0.72 g of N,N-dimethylbenzylamine was added and reacted for 10 hours with stirring, and the reaction was terminated when a peak of the Rf epoxy in gas chromatography disappeared. After the reaction was finished, the polymer was poured onto a vat, cooled to be solidified, and ground to give powder.

Synthesis Example 4

[0071] 876 g of the Rf epoxy (the same as in Synthesis Example 3), 31 g of succinic anhydride and 104 g of phthalic anhydride were introduced into a 1.5 L glass reaction vessel and heated to 140°C in an oil bath. 1.00 g of N,N-dimethylbenzylamine was added and the mixture was reacted for 15 hours with stirring. The reaction was terminated when a peak of the Rf epoxy in gas chromatography disappeared. After the reaction was finished, the polymer was poured onto a vat, cooled to be solidified, and ground to give powder.

Example 5

[0072] 4.0 parts of a polytetrafluoroethylene low-molecular weight polymer [Lubron L-5, manufactured by Daikin Industries Ltd.] (weight average molecular weight of about 300,000) and 2.0 parts of the polyfluoroalkyl group-containing polymer prepared in Synthesis Example 3 were added to 100 parts of a phenol resin (PM840J, manufactured by Sumitomo Bakelite Co., Ltd.) as thermosetting resin and sufficiently kneaded in a kneader and uniformly dispersed in the resin. Then, this resin was molded under the conditions of a die temperature of 165°C and a curing rate of 3 minutes whereby a molded article of 5 cm square and 0.3 cm in thickness was obtained. This molded article was thermally treated at 100°C for 1 hour and measured for contact angle toward water and n-hexadecane. The results are shown in Table 1.

Example 6

[0073] 4.0 parts of polytetrafluoroethylene low-molecular weight polymer [Lubron L-5, manufactured by Daikin Industries Ltd.] (weight average molecular weight of about 300,000) and 2.0 parts of the polyfluoroalkyl group-containing polymer in Synthesis Example 4 were added to 100 parts of an unsaturated polyester resin (AP301B, manufactured by Toshiba Chemical) and sufficiently kneaded in a kneader and uniformly dispersed in the resin. Then, this resin was molded under the conditions of a die temperature of 145 °C and a curing rate of 3 minutes whereby a molded article of 5 cm square and 0.3 cm in thickness was obtained. This molded article was thermally treated and then measured for contact angle in the same manner as in Example 5. The results are shown in Table 1.

Comparative Example 4

[0074] The phenol resin was cured and measured for contact angle in the same manner as in Example 5 except that both of polytetrafluoroethylene and the compound prepared in Synthesis Example 3 were not added. The results are shown in Table 1.

Comparative Example 5

[0075] The unsaturated polyester resin was cured and measured for contact angle in the same manner as in Example 6 except that the polytetrafluoroethylene and the compound prepared in Synthesis Example 4 were not added. The results are shown in Table 1.

Table 1

	Impact Energy N/cm (kgf·cm)	Flame Retardance		Contact Angle (°)		Specific Abrasion Wear ($\times 10^{-5} \text{cm}^3 \cdot$ $\text{sec/kg} \cdot \text{m} \cdot$ hr)	Flux Barrier Properties
		V Class	Number of Droplets	Water	n- Hexadecane		
Example 1	314 (32)	V-0	0/10	-	-	-	-
Comparative Example 1	127 (13)	V-0	0/10	-	-	-	-
Example 2	510 (52)	-	-	90°	44°	263	-
Example 3	530 (54)	-	-	89°	44°	223	-
Comparative Example 2	118 (12)	-	-	74°	22°	320	-
Example 4	216 (22)	V-0	0/10	105°	48°	-	○
Comparative Example 3	78 (8)	V-0	0/10	76°	24°	-	×
Example 5	-	-	-	88°	53°	-	-
Example 6	-	-	-	86°	56°	-	-
Comparative Example 4	-	-	-	76°	14°	-	-
Comparative Example 5	-	-	-	74°	16°	-	-

EFFECTS OF THE INVENTION

[0076] The resin composition of the present invention contains the polyfluoroalkyl group-containing polymer which is compatible with both the fluorine-free resin and the fluorine-containing resin added for conferring the flame re-

tardance, dripping-preventing properties and sliding properties on said fluorine-free resin, thus giving a molded article excellent in impact resistance. Further, the resin composition of the present invention is excellent in water- and oil-repellency, thus attaining the effect of repelling flux. This repellency is considered attributable to transfer of the polyfluoroalkyl group-containing polymer to the surface of a molded article after molding the resin composition.

Claims

1. A resin composition comprising:

- (a) a fluorine-free thermoplastic resin,
- (b) a fluorine-containing resin which is a homopolymer, modified polymer or core/shell polymer of tetrafluoroethylene, and
- (c) a polyfluoroalkyl group-containing polymer which is (i) a homopolymer or copolymer of polyfluoroalkyl group-containing (meth)acrylate or (ii) a polyfluoroester.

2. The resin composition according to claim 1, which comprises (d) a flame-retardant.

3. A resin molded article comprising the resin composition of claim 1.

4. The resin molded article according to claim 3, wherein the resin composition comprises (d) a flame-retardant.

5. The resin molded article according to claim 3 or 4, wherein the resin composition is molded and then thermally treated at 70 to 130°C.

Patentansprüche

1. Harzzusammensetzung, umfassend:

- (a) ein fluorfreies thermoplastisches Harz,
- (b) ein fluorhaltiges Harz, das ein Tetrafluorethylenhomopolymer, ein modifiziertes Tetrafluorethylenpolymer oder ein Kern/Schalenpolymer des Tetrafluorethylens ist, und
- (c) ein Polyfluoralkyl-haltiges Polymer, das

- (i) ein Homopolymer oder Copolymer eines Polyfluoralkyl-haltigen (Meth)Acrylats oder
- (ii) ein Polyfluorester ist.

2. Harzzusammensetzung gemäß Anspruch 1, die (d) ein Flammenschutzmittel umfaßt.

3. Ein aus Harz geformter Gegenstand, der die Harzzusammensetzung des Anspruchs 1 umfaßt.

4. Der aus Harz geformte Gegenstand gemäß Anspruch 3, worin die Harzzusammensetzung (d) ein Flammenschutzmittel umfaßt.

5. Der aus Harz geformte Gegenstand gemäß Anspruch 3 oder 4, worin die Harzzusammensetzung geformt und dann bei 70 bis 130°C thermisch behandelt wird.

Revendications

1. Composition de résine comprenant

- (a) une résine thermoplastique sans fluor,
- (b) une résine fluorée qui est un homopolymère, un polymère modifié ou un polymère noyau/enveloppe du tétrafluoroéthylène, et
- (c) un polymère contenant des groupes polyfluoroalkyle qui est (i) un homopolymère ou copolymère de (méth)acrylate contenant un groupe polyfluoroalkyle ou (ii) un polyfluoroester.

EP 0 930 338 B1

2. Composition de résine selon la revendication 1 qui comprend (d) un ignifugeant.
3. Article moulé en résine comprenant la composition de résine selon la revendication 1.
- 5 4. Article moulé en résine selon la revendication 3 où la composition de résine comprend (d) un ignifugeant.
5. Article moulé en résine selon la revendication 3 ou 4 où la composition de résine est moulée puis traitée thermiquement à 70 à 130°C.

10

15

20

25

30

35

40

45

50

55